

DEVELOPMENT OF ADVANCED LITHIUM-ION RECHARGEABLE CELLS WITH IMPROVED LOW TEMPERATURE PERFORMANCE

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ABSTRACT

Due to future plans to explore Mars and the outer planets, NASA has interest in developing lithium-ion rechargeable batteries that are capable of operating at low temperatures. To address these problems, we have initiated research focused upon the development of advanced electrolyte systems for lithium-ion cells with improved low temperature performance. Promising electrolyte solutions were selected based on conductivity and stability considerations and incorporated into C/LiCoO₂ cells for evaluation. The discharge capacity and rate capability as a function of temperature were evaluated in two types of lithium-ion cells, consisting of graphite-based systems with EC-based electrolytes and coke-based systems with PC-based electrolytes. Some of the experimental lithium-ion cells fabricated with these electrolytes were found to be capable of operating at temperatures as low as -30°C (both charging and discharging at -30°C) and provide more than 55% of the room temperature capacity. Cycle life testing of these cells at -20°C and at room temperature is in progress. Some of the cells have completed more than 500 cycles to date (100% DOD).

INTRODUCTION

Lithium-ion cells generally show poor performance at low temperatures. This poor performance is primarily due to the limitations of the electrolyte solutions which contain organic solvents, such as ethylene carbonate (EC) and dimethyl carbonate (DMC), that become highly viscous and freeze at low temperatures resulting in poor conductivity of the medium. Thus, recently there has been interest in developing electrolytes which can result in lithium-ion cells with improved low temperature performance. (Ein-Eli, 1997; Juzkow, 1997)

In designing electrolytes that are highly conductive at low temperatures it is necessary to

consider a number of important parameters, such as the dielectric constant of the medium, the viscosity, the Lewis acid-base coordination behavior, as well as the appropriate liquid ranges and salt solubilities of the systems. For an electrolyte solution to be a viable candidate for lithium-ion cell applications, it must satisfy a number of requirements in addition to possessing the desired conductivity over the specified temperature range, such as (i) possess good electrochemical stability over a wide voltage window (0 to 4.5V), (ii) have the ability to form thin, stable passivating films at the carbonaceous anode electrode, and (iii) display good thermal and chemical stability. All of these factors need to be weighed accordingly depending on the ultimate application intended.

An effective way to improve the low temperature conductivity of the electrolyte solution is to extend the liquid range and decrease the viscosity of the solvent system used. This can be accomplished by the addition of solvents which improve the low temperature conductivity of EC and PC-based systems. Possible candidate solvent additives include formates, acetates, cyclic and aliphatic ethers, lactones, as well as other carbonates, such as diethyl carbonate (DEC). In addition, an optimization of the electrolyte salt concentration can also translate into improved low temperature conductivity. We have previously identified (Smart, 1996) a number of electrolytes which are highly conductive at low temperatures based upon these approaches and successfully demonstrated their use in lithium-ion cells.

After evaluating the low temperature conductivity and assessing the relative stability of potential systems, a number of electrolytes were selected for evaluation in lithium-ion experimental cells. The low temperature and cycle life performance of these cells was the basis for selecting six electrolytes for incorporation into prototype cells which were fabricated by Wilson Greatbatch Ltd. according to

JPL design and possessing electrolytes and electrode materials prepared at JPL.

The electrolytes chosen for integration into the prototype cells consist of three ethylene carbonate-based solutions for use with graphite-type anodes: 1.0 M LiPF₆ EC+ DMC(30:70), 1.0 M LiPF₆ EC+ DEC (30:70), and 1.0 M LiPF₆ EC+ DEC+ DMC (1:1:1), and three propylene carbonate-based electrolytes for use with coke-type anodes: 1.0 M LiPF₆ PC+ DEC (50:50), 0.5 M LiPF₆ PC+ DEC (25:75), and 0.5 M LiPF₆ PC+ DME (50:50).

EXPERIMENTAL

The specific conductivity of a number of electrolyte solutions was measured over the temperature range of -60°C to 25°C using a conductivity cell which consists of two platinized platinum electrodes which are immobilized in a glass apparatus and separated by a fixed distance. The cell constant of the apparatus was determined by comparing the resistivity of a 0.1 M KCl solution with the value reported in the literature. Using an a.c. impedance analyzer, the bulk resistivity was measured from which the specific conductivity was calculated once the cell constant has been determined. The temperature was controlled in these experiments by utilizing a Tenney environmental low temperature chamber (+/- 1 °C).

The candidate electrolytes were evaluated in both 150-300 mAh size in-house experimental test cells and AA size prototype cells fabricated by Wilson Greatbatch Ltd. (Greatneck, New York) according to JPL design and containing materials prepared by JPL. These cells were fabricated with LiCoO₂ as the cathode material and coke or graphite as the anode materials. These cells were evaluated for rate capability, low temperature performance and cycle life. Cells were charged at constant current to 4.1 V and constant voltage to a taper current of -C/100, and discharged at various rates to 3.0V, unless otherwise stated. Data were collected using an Arbin battery test system.

RESULTS AND DISCUSSION

Electrolyte Conductivity

It had been previously identified that high EC or DMC content in electrolyte solutions generally results in poor low temperature conductivity due to their high melting points and viscosities. The low temperature conductivity can, therefore, be improved by substituting these solvents with carbonates of lower melting points, such as PC or DEC, or by the addition of a third component which can serve as a low viscosity additive. For example, electrolytes composed of EC + DEC and EC + DEC + DMC both display higher conductivity at lower temperature due to the use of DEC which has a lower melting point and a lower viscosity, as shown in Table 1.

In addition to selecting the appropriate solvent mixtures, the lithium-salt concentration needs to be optimized for low temperature operation. Although high salt concentrations generally translate into high conductivity at ambient temperatures and can also depress the freezing point of the solvent system, the conductivity at low temperature is poor due to increased viscosity and ion-pairing phenomena. In contrast, electrolytes with lower salt concentrations generally display higher conductivities at low temperatures. This trend arises from the fact that the electrolyte concentration of the conductivity maximum decreases uniformly with decreasing temperature. (Barthel, 1971 and Gores, 1980) For this reason, two of the PC-based electrolytes were based upon lower salt concentrations than customarily employed with the expectation of enhanced cell performance at temperatures below -20°C.

TABLE 1
Specific conductivity of EC- and PC-based electrolytes from -60° to 25°C.

Electrolyte Concentration	Solvent System	Conductivity (mS/cm)			
		-60°	-40°	-20°	0°C R.T.
1.0 M LiPF ₆	EC + DMC (30:70)	Fr.	0.66	1.9	7.1
1.0 M LiPF ₆	EC + DEC (30:70)	Fr.	0.66	1.9	4.0
1.0 M LiPF ₆	EC + DEC + DMC (1:1:1)	0.02	1.0	2.9	5.6
0.5 M LiPF ₆	PC + DEC (25:75)	0.28	0.97	2.1	3.7
1.0 M LiPF ₆	PC + DEC (50:50)	0.05	0.4	1.6	3.6
0.5 M LiPF ₆	PC+ DME (50:50)	0.67	2.3	4.6	7.6

Discharge Capacity at Different Rates and Temperatures

A number of cells were fabricated with each electrolyte and evaluated in terms of the discharge characteristics and rate capability as a function of temperature. A comparison of the low temperature discharge performance of graphite-based cells at -20°C, (Fig. 1), shows that the cells containing the electrolyte 1.0 M LiPF₆ EC + DEC + DMC (1:1:1) delivered the highest capacity at -20°C, corresponding to over 850% of the room temperature capacity. The discharge characteristics observed for cells at -20°C correlate well with the conductivity trend: EC+ DEC+ DMC > EC + DEC > EC + DMC. A significant aspect of these measurements is that both the charge and discharge were performed at low temperature, in contrast to charging at ambient conditions and only discharging at low temperature. From the experimental results, it is evident that the

incorporation of DEC into the solvents mixtures can greatly improve the low temperature performance compared to the SOA EC + DMC-based electrolyte systems.

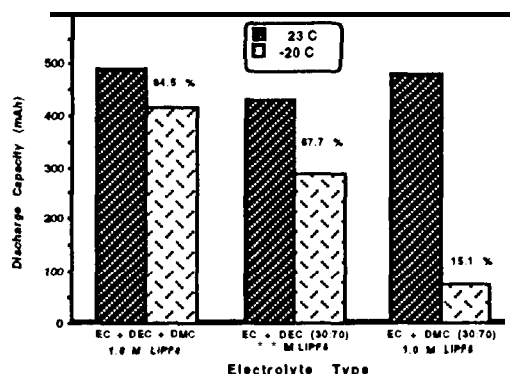


Fig. 1. Comparison of the discharge capacities of graphite-based JPL/WGL AA-size lithium-ion cells as a function of temperature.

The discharge capacities of the cells were evaluated over a temperature range of -40° to 23°C and at a number of different charge and discharge rates. As shown in Fig. 2, the discharge capacity of a cell containing 1.0 M LiPF₆ EC + DEC + DMC (1:1:1) electrolyte was evaluated over a large temperature range and was observed to deliver ~60% of the room temperature capacity at -30°C at -C/20 rate. Graphite-based prototype cells containing this ternary electrolyte displayed the best low temperature performance of the EC-based systems studied.

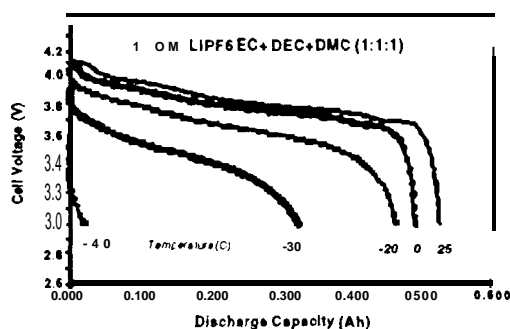


Fig. 2. Discharge capacity of JPL/WGL lithium-ion cell containing 1.0 M LiPF₆ EC + DEC + DMC (1:1:1) electrolyte as a function of temperature. Cell was charged at rate of 25mA (-C/20) to 4.1 V and discharged at a rate of 25mA (-C/20) to 3.0V.

As expected, the rate capability of the cells decreased with decreasing temperature. However, as illustrated in Fig. 3, a cell containing 1.0 M LiPF₆ EC +

DEC + DMC (1:1:1) and discharged at a rate of -C/5 at -20°C was still capable of delivering 70% of the capacity displayed at a C/20 rate.

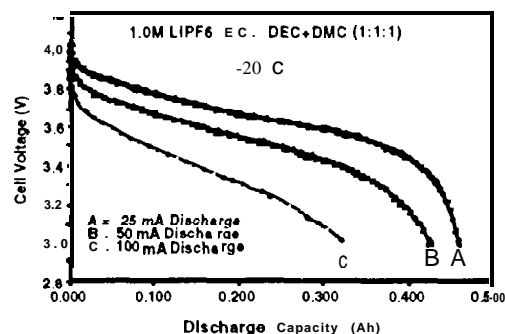


Fig. 3. Rate capability of JPL/WGL lithium-ion cell at -20°C containing 1.0 M LiPF₆ EC + DEC + DMC (1:1:1) electrolyte. Cell was charged at -20°C at a rate of 25mA (-C/20) to 4.1 V and discharged at -20° at various rates to 3.0V.

When the low temperature performance of the coke-based prototype cells was evaluated at -20°C and at a discharge rate of -C/8 (Fig. 4), both 0.5 M LiPF₆ PC + DEC (25:75) and 0.5 M LiPF₆ PC + DME (50:50) showed similar performance and both were slightly better than the cells with 1.0 M LiPF₆ PC + DEC (50:50).

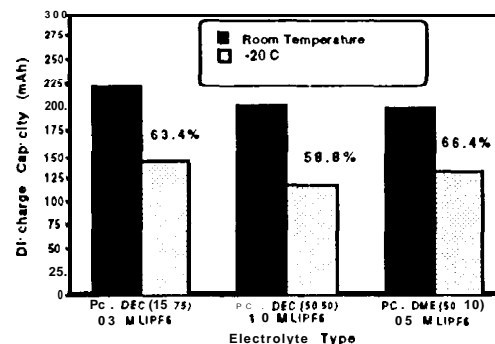


Fig. 4. Comparison of the discharge capacities of coke-based JPL/WGL AA-size lithium-ion cells as a function of temperature.

As shown in Fig. 5, the coke cells containing 0.5 M LiPF₆ PC + DEC (25:75) electrolyte performed well at low temperature, with 69% of the room temperature capacity delivered at -20°C and 490% of the capacity at -30°C at rate of greater than C/8.

When the discharge capacities of both the coke-type and graphite-type design prototype cells were evaluated at -30°C under the same rate conditions (Fig. 6), the cell containing 1.0 M LiPF₆ EC + DMC +

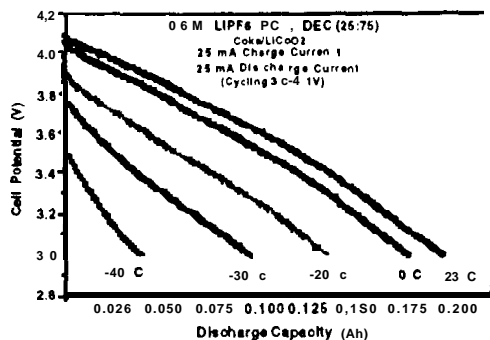


Fig. 5. Discharge capacity of JPL/WGL lithium-ion cell containing 0.5 M LiPF₆ PC + DEC (25:75) electrolyte as a function of temperature. Cell was charged at rate of 25mA (-C/8) to 4.1 V and discharged at a rate of 25mA (-C/8) to 3.0V.

DEC (1:1:1) out-performed all other systems dramatically. The high capacity of this system is attributed to the high conductivity of the electrolyte at low temperature and the inherently high capacity of graphite compared to coke-based systems.

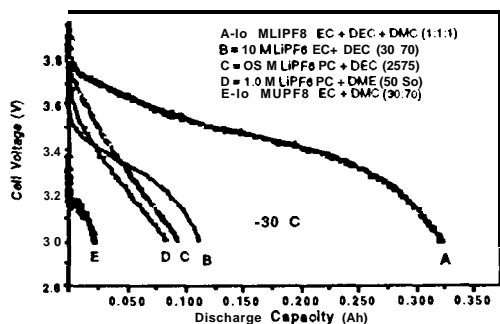


Fig. 6. Comparison of EC and PC based electrolytes at -30°C. Cells were cycled at a charge rate of 25 mA and a discharge rate of 25mA between 3.0 and 4.1 V.

When the cells are compared at -40°C in terms of the observed discharge capacity, the PC/coke-based systems show improved performance over that of the EC/graphite-based systems, as illustrated in Fig. 7. The delivered discharge capacity can be increased greatly at low temperatures if low rates are used and the discharge cut-off voltage is lowered below 3.0V. As shown in Fig. 8, when the discharge cut-off voltage is lowered to 2.5V and the discharge rate decreased from 25mA to 10mA the discharge capacity is increased by a factor of three to four in the systems studied. Although it has been suggested that continued discharge to low voltage may promote cell degradation mechanisms, the processes are likely to be less significant at lower temperatures due to

change in electrode potential as a function of temperature and slower reaction kinetics.

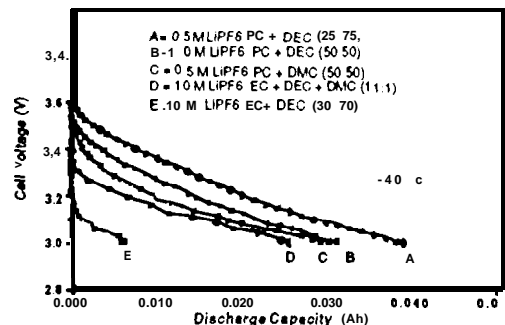


Fig. 7. Comparison of EC and PC based electrolytes at -40°C Cells were charged at 25mA and discharged at 25mA.

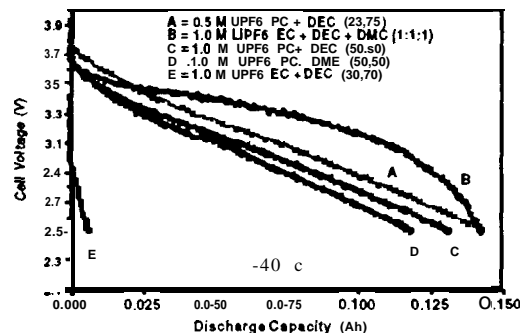


Fig. 8. Comparison of EC and PC based electrolytes at -40°C. Cells were charged with a 10mA charge current to 4.1 V and discharged at a 10mA rate to 2.5V.

When the cells were evaluated at extremely low temperatures (-58°C), at very low rates (C/70 to C/150) and discharged to 2.0V, the cell containing 1.0 M LiPF₆ EC + DMC + DEC (1:1:1) electrolyte was observed to deliver > 460 mAh capacity, which corresponds to > 900% of the room temperature capacity, as shown in Fig. 9.

Cycle Life Performs.ca

In addition to evaluating the rate performance as a function of temperature, the cycle life performance was assessed at both room temperature and at -20°C. Although the primary focus of the Mars Exploration Program is to develop a rechargeable battery capable of operation at low temperature, room temperature cycling tests were deemed necessary to demonstrate the requisite stability during storage, launch, cruise or during daylight hours on Mars. The room temperature

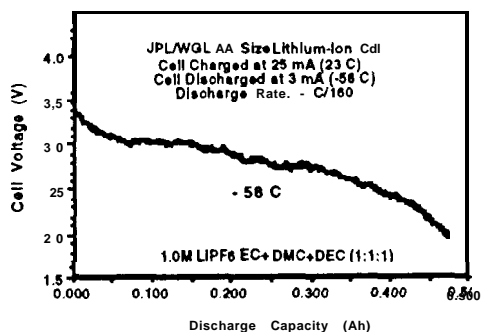


Fig. 9 Discharge capacity of cell containing 1.0 M LiPF_6 EC + DMC + DEC (1:1:1) electrolyte at -58°C using a discharge current of 3mA.

cycling tests of a number of cells are currently in progress, and the graphite-based AA size cells have completed > 200 cycles to date, as shown in Fig. 10. The results suggest that all three electrolyte systems will provide > 300 cycles with minimal capacity fade, which satisfies the Mars Exploration Program requirements for a number of missions.

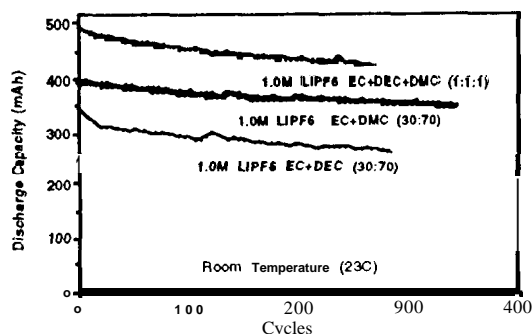


Fig.10. Room temperature cycle life performance of graphite-based AA size Li-ion cells. Cells were charged at rate of 50mA (-C/10) and discharged at a rate of 100mA (-C/5).

To assess the low temperature cycle life performance of the various systems, both experimental and prototype cells were cycled at -20°C (100% DOD) with both charge and discharge performed at low temperature. Initial studies of PC-based electrolyte systems lead to the identification of 0.5 M LiPF_6 PC + DEC (25:75) as a promising low temperature electrolyte. We have recently demonstrated more than 750 cycles at -20°C with an experimental lithium-ion cell containing this electrolyte, as shown in Fig. 11. The specific energy and the discharge capacity were increased without a large impact on the capacity fade characteristics at -20°C when a higher cathode/anode ratio is selected

in the cell design, as illustrated in Fig.12.

The low temperature cycle life performance of the prototype cells fabricated by WGL correlate well with data obtained with experimental cells. As illustrated in Fig. 13, the cells containing 0.5 M LiPF_6 PC + DEC (25:75) and 0.5 M LiPF_6 PC + DME (50:50) have successfully completed >250 cycles at -20°C with minimal capacity fade.

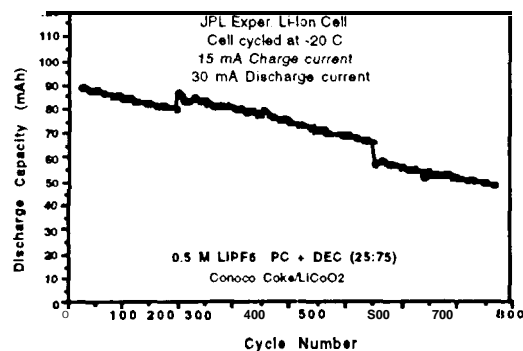


Fig. 11. Low temperature cycle life performance (at -20°C) of experimental lithium-ion coke-based cell containing 0.5 M LiPF_6 PC + DEC (25:75) electrolyte. Cell was charged at rate of 15mA (-C/10) and discharged at a rate of 30mA (-C/5).

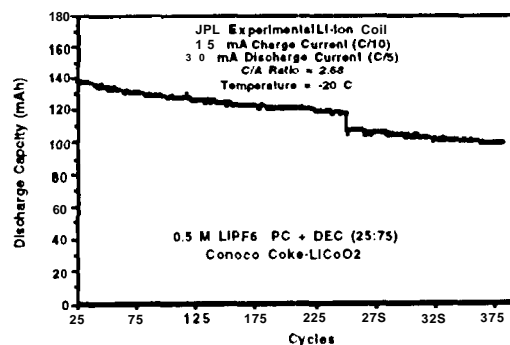


Fig. 12. Low temperature cycle life performance (at -20°C) of experimental lithium-ion coke-based cell containing 0.5 M LiPF_6 PC + DEC (25:75) electrolyte. Cells were charged at rate of 15mA (-C/10) and discharged at a rate of 30mA (-C/5).

The best cycle life at low temperature observed with graphite-based system-s was with 1.0 M LiPF_6 EC + DMC + DEC (1:1:1) electrolyte, which initially delivered > 84% of the room temperature capacity at -20°C and displayed >75 Wh/Kg at a C/10 rate, as shown in Fig. 14. The cells containing 1.0 M LiPF_6 EC + DMC (30:70) and 1.0 M LiPF_6 EC + DEC (30:70) both showed inferior behavior with lower capacities and higher capacity fade rates.

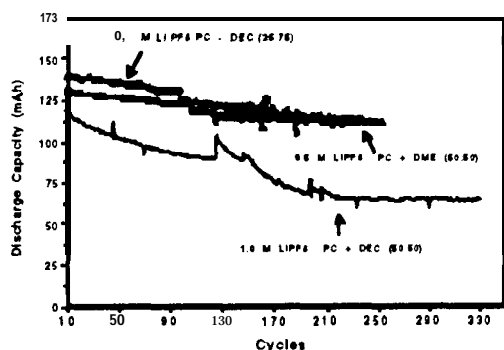


Fig.13. Low temperature cycle life performance (at -20°C) of JPL/WGL lithium-ion coke-based cells containing :0.5 M LiPF_6 PC+ DEC (25:75), 1.0 M LiPF_6 PC+ DEC (50:50), and 0.5 M LiPF_6 PC+ DME (50:50) electrolytes. Cells were charged at rate of 25mA (-C/10) to 4.1 V and discharged at a rate of 50mA (-C/5) to 3.0V.

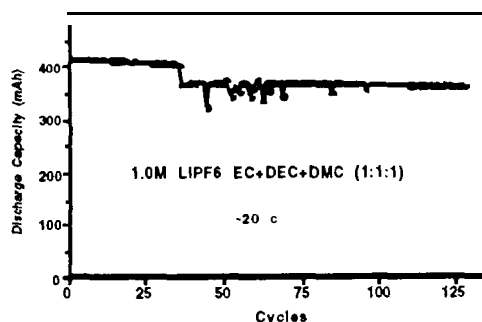


Fig.14. Low temperature cycle life performance (at -20°C) of JPL/WGL lithium-ion cell containing 1.0 M LiPF_6 EC + DMC + DEC (1:1:1) electrolyte. Cell was charged at rate of 25mA (-C/20) and discharged at a rate of 50mA (-C/10).

Conclusion

We have identified a number of promising electrolyte systems for lithium-ion cells with improved low temperature performance. For the graphite-based systems studied, the prototype cells containing 1.0 M LiPF_6 EC+ DMC + DEC (1:1:1) electrolyte showed the best performance. In considering the coke-based systems with PC electrolytes, all three of the electrolytes performed comparably with 0.5 M LiPF_6 PC + DEC (25:75) exhibiting the best discharge capacities and cycle life performance. A large improvement in the capacity of the cells at low temperatures was observed upon discharging to voltages below 3.0V. At very low temperatures (-58°C), large discharge capacities were observed

with low rates and low discharge cut-off voltages. We have demonstrated good cycle life at both room temperature and at -20°C with graphite-based and coke-based cells.

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